(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 816 065 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
07.01.1998 Bulletin 1998/02

(21) Application number: **96900440.7**

(22) Date of filing: **12.01.1996**

(51) Int. Cl.[6]: **B32B 18/00**, F01N 3/02

(86) International application number:
PCT/JP96/00042

(87) International publication number:
WO 97/25203 (17.07.1997 Gazette 1997/31)

(84) Designated Contracting States:
DE DK FR IT SE

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(54) CERAMIC STRUCTURE

(57) As a ceramic structural body improving material properties of a sealing member such as adhesion properties at room temperature and high temperature and the like and having an improved durability, there is proposed a ceramic structural body comprising an assembly of plural united ceramic members 2, 3 each having a plurality of through-holes arranged side by side along a longitudinal direction, in which end faces at either side of these through-holes are closed in a checkered pattern so as to have a reverse relation of open and close between gas inlet side and gas outlet side and adjacent through-holes are permeable to each other through porous partition walls, characterized in that a plurality of the ceramic members 2, 3 are integrally adhered by interposing a sealing member 4 of an elastic material consisting of at least inorganic fibers, an inorganic binder, an organic binder and inorganic particles and mutually bonded three-dimensionally intersected organic fibers and inorganic particles through the inorganic binder and organic binder between the mutual ceramic members.

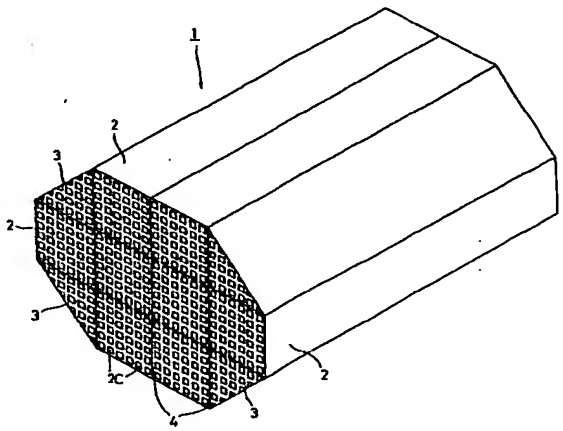

Fig. 1

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Particularly, in order to form a large-size divided ceramic structural body, a larger restraint force is required, the combination of the conventional non-adhesion sealing member and thermally expansive heat insulator cannot deal with from the beginning, so that there is not obtained the structural body withstanding to practical use.

Under the above circumstances, the inventors have previously proposed "EXHAUST GAS PURIFYING APPARATUS AND STRUCTURAL BODY THEREOF" with the use of a sealing member consisting of ceramic fiber, silicon carbide powder and inorganic binder by improving the sealing member constituting the divided ceramic structural body as means for overcoming the problems inherent to the above conventional technique (see Japanese Patent Application No. 5-204242).

According to this proposal, a plurality of ceramic members are joined to each other through such a sealing member, so that it is possible to improve the durability of the divided ceramic structural body to a certain extent.

However, the sealing member tends to easily cause migration (phenomenon of moving a binder with drying and removal of a solvent) when it is filled and cured between the mutual ceramic members. Therefore, the seal layer formed by curing the sealing member becomes brittle.

That is, the inorganic binder constituting the above sealing member acts to firmly join the ceramic member to the seal layer and to join an intersect point of three-dimensionally crossed ceramic fibers as an important element for developing stress buffering function of the seal layer. However, the inorganic binder moves from the inside of the seal layer to the joint face with the ceramic member through the migration produced in the course of drying and curing, whereby the joint force at the intersect point is decreased, and hence the strength of the ceramic structural body itself is lowered, so that the desired durability could not be satisfied.

Furthermore, the silicon carbide powder constituting the sealing member also moves with the above migration to bring about the lowering and nonuniformity of thermal conductivity, which results in the lowering of the regeneration efficiency of the ceramic structural body.

On the contrary, there is considered a method of improving the durability of the structural body by controlling the migration. However, this method takes a long time for drying and curing the sealing member ant undesirably degrades the productivity.

As mentioned above, the conventional divided ceramic structural body still leaves room for improvement with respect to durability and the like as a ceramic structural body.

The invention is made for solving the above-described various problems inherent to the conventional technique, and its main object is to improve the durability of the ceramic structural body.

Another object of the invention is to improve material properties such as adhesion properties of a sealing member at room temperature and high temperature and the like.

The other object of the invention is to improve the adhesion property and thermal conductivity of the sealing member at room temperature and high temperature while maintaining elasticity and heat resistance to thereby simultaneously improve both durability and regeneration efficiency of the divided ceramic structural body.

DISCLOSURE OF THE INVENTION

The inventors have made further studies to realize the above objects. As a result, the inventors have found an invention having the construction mentioned below.

That is, the invention lies in a ceramic structural body comprising an assembly of plural united ceramic members each having a plurality of through-holes arranged side by side along a longitudinal direction, in which end faces at either side of these through-holes are closed in a checkered pattern so as to have a reverse relation of open and close between gas inlet side and gas outlet side and adjacent through-holes are permeable to each other through porous partition walls, characterized in that a plurality of the ceramic members are integrally adhered by interposing a sealing member of an elastic material consisting of at least inorganic fibers, an inorganic binder, an organic binder and inorganic particles and mutually bonded three-dimensionally intersected organic fibers and inorganic particles through the inorganic binder and organic binder between the mutual ceramic members.

The sealing member is desirable to be an elastic material formed by using ceramic fiber as the inorganic fiber, using colloidal sol as the inorganic binder, using polysaccharide as the organic binder, and using at lease one inorganic powder or whisker selected from carbides and nitrides as the inorganic particle, and mixing them each other. Particularly, the sealing member is desirable to be an elastic material formed by using at least one ceramic fiber selected from silica-alumina, mullite, alumina and silica as the inorganic fiber, using at least one colloidal sol selected from silica sol and alumina sol as the inorganic binder, using at least one polysaccharide selected from polyvinyl alcohol, methyl cellulose, ethyl cellulose and carboxymethyl cellulose as the organic binder and using at least one inorganic powder or whisker selected from silicon carbide, silicon nitride and boron nitride as the inorganic particle. More particularly, it is desirable to be an elastic material consisting of silica-alumina ceramic fiber, silica sol, carboxymethyl cellulose and silicon carbide powder.

Concretely, the above sealing member is favorable to have the following composition.

inorganic binder can hold the adhesion strength even at the low temperature region through drying and heating.

Therefore, the ceramic structural body having excellent adhesion strengths at low temperature region and high temperature region can be formed by a synergistic action of the organic binder with the above effect of entangling the ceramic fibers such as silica-alumina with the inorganic binder such as silica sol.

A third point lies in that the inorganic particles are existent on the surface of the inorganic fiber and the surface of the inorganic binder or the inside thereof to improve the thermal conductivity of the ceramic structural body.

Particularly, inorganic particle such as nitride and carbide can considerably improve the thermal conductivity owing to a high thermal conductivity property inherent to the nitride and carbide.

Therefore, the sealing member containing the inorganic particles is excellent in the thermal conductivity and can effectively prevent the breakage of the ceramic structural body without causing temperature peak phenomenon at the regeneration while filling gaps produced in the combination of plural ceramic members when the sealing member is used, for example, as a filter for an exhaust gas purifying apparatus. Moreover, the occurrence of cracks by heat cycle can be reduced, and the edge portion of the outer periphery of the filter can be heated in a relatively short time to improve the regeneration efficiency.

The ceramic structural body according to the invention will be described in detail as follows.

When the ceramic structural body is used as a filter for an exhaust gas purifying apparatus, the sealing member constituting the structural body is necessary to have elasticity, thermal conductivity, joining property, strength and the like in addition to heat resistance. When the elasticity is excellent, even if thermal stress is applied to the filter by heating, this thermal stress can surely be liberated. Further, when the thermal conductivity is excellent, heat of a heating element is immediately and evenly conducted to the whole of the structural body, and the temperature difference in the exhaust gas purifying apparatus is minimized. Moreover, when the joining property and strength are excellent, the adhesion property between the adjacent united ceramic members becomes excellent, and the durability of the ceramic structural body itself becomes excellent.

The invention lies in that the construction of the sealing member exhibiting the above properties is an elastic structural body formed by using the inorganic fibers, inorganic binder, organic binder and inorganic particles and mutually bonding the three-dimensionally intersected inorganic fibers and inorganic particles through the inorganic binder and organic binder.

As the inorganic fiber, there are silica-alumina ceramic fiber, mullite fiber, alumina fiber and silica fiber. Particularly, the silica-alumina ceramic fiber is desirable because it is excellent in the elasticity and shows a function of absorbing thermal stress.

As the inorganic binder, colloidal sol is desirable, which includes, for example, alumina sol and silica sol. Particularly, silica sol is desirable, which acts as an adhesive (inorganic binder). This silica sol is easily available and suitable as an adhesive at high temperature region because it is easily changed into SiO_2 by firing, and is excellent in the insulating property.

As the organic binder, a hydrophilic organic high polymer is desirable, and particularly polysaccharide is more preferable. Concretely, there are polyvinyl alcohol, methyl cellulose, ethyl cellulose, carboxymethyl cellulose and the like. Among them, carboxymethyl cellulose is particularly desirable because it secures the fluidity at the time of assembling (contributes to improvement of workability) and shows an excellent adhesion property at room temperature region.

As the inorganic particle, inorganic particles of carbide and/or nitride are desirable, such as silicon carbide, silicon nitride and boron nitride. These carbide and nitride are very large in the thermal conductivity and contribute to the improvement of the thermal conductivity by existing on the surface of ceramic fiber and the surface and inside of colloidal sol. For example, the thermal conductivity of silicon carbide is 0.19 cal/cm • sec • °C, and the thermal conductivity of boron nitride is 0.136 cal/cm • sec • °C, while the thermal conductivity of alumina is about 0.08 cal/cm • sec • °C, so that it is understood that the carbide and nitride are particularly effective for improving the thermal conductivity.

Among the inorganic particles of these carbide and nitride, silicon carbide is particularly optimum in view of the thermal conductivity. Boron nitride is lower than silicon carbide in the affinity with ceramic fiber. That is, silicon carbide possesses all of adhesion property, heat resistance, water resistance and thermal conductivity.

An embodiment of using the ceramic structural body according to the invention in a filter for an exhaust gas purifying apparatus attached to a diesel engine will be described in detail with reference to Figs. 1~5 below.

Fig. 1 shows a filter 1 for an exhaust gas purifying apparatus using the ceramic structural body according to the invention, and Fig. 2 is a partially enlarged section view of the filter. In these figures, the filter 1 for the exhaust gas purifying apparatus is constructed by integrally adhering eight prismatic ceramic members 2 and four ceramic members 3 of a right angle equilaterally triangle in section through sealing members 4 (1.5~3.0 mm in thickness) of an elastic material interposed between the mutual members.

Figs. 3~5 show the ceramic member 2 constituting a part of the filter for the exhaust gas purifying apparatus. In these figures, through-holes 2a of an approximately square shape in section are regularly pierced in the ceramic member 2 of a prismatic shape (33 mm × 33 mm × 150 mm) along its axial direction. These through-holes 2a are separated from each other with porous partition walls 2b of 0.3 mm in thickness. Either one end of exhaust gas inlet side and outlet

Moreover, the above sealing member caused migration at the time of drying and curing.

The evaluation of performances with respect to the filters 1 prepared in Examples 1~3 and Comparative Example was carried out by the following method.

[Measurement of adhesion strength at initial stage and after heat cycle]

As shown in Fig. 6, a test piece corresponding to three ceramic members was cut from the filter 1 and a load was applied to a central ceramic member to measure a load causing the peeling. Moreover, since quick heating and quenching from room temperature to 900°C were anticipated in actual use, the test piece was subjected to a heat cycle test of room temperature ~ 900°C.

Table 1 shows results measured on the adhesion strength at an initial stage and after heat cycle (after 100 cycles) between the mutual ceramic members 2, 3 constituting the filter 1. Moreover, the reason why the strength after heat cycle is improved is assumed due to the sintering action of silica by heating at 900°C.

Table 1

	Adhesion strength at initial stage	Adhesion strength after heat cycle
Example 1	4.6 kg/cm^2	7.6 kg/cm^2
Example 2	4.5 kg/cm^2	5.3 kg/cm^2
Example 3	4.3 kg/cm^2	5.6 kg/cm^2
Comparative Example 1	2.3 kg/cm^2	0.76 kg/cm^2

[Measurement of thermal conductivity]

As shown in Fig. 7, a test piece corresponding to four ceramic members was cut out and covered on its outer periphery with a heat insulator and placed on a heater 6 to conduct heating for 20 minutes. A temperature difference between T1 and T2 was measured.

Table 2 shows results measured on the temperature difference between T1 and T2 shown in Fig. 7 with respect to Examples 1~3 and Comparative Example.

Table 2

	T1-T2 temperature difference
Example 1	55°C
Example 2	65°C
Example 3	70°C
Comparative Example	180°C

As seen from the above results, the filter using the ceramic structural body according to the invention has considerably high adhesion strength even at both high temperature and room temperature, and is excellent in the heat cycle property, so that it was confirmed that the durability as a filter is excellent.

And also, this ceramic structural body is excellent in the thermal conductivity, so that the occurrence of peak temperature in the ceramic member located inside the filter can be reduced and also the temperature rising time of the ceramic structural body located at the edge portion can be shortened and hence the improvement of the regeneration efficiency can simultaneously be realized.

Moreover, the construction of the filter 1 applying the ceramic structural body according to the invention is not limited to those described in the above examples, and can be changed to the following construction. For example,

(a) The number of combined ceramic members is not necessarily 12 as in the examples, but any optional number is possible. In this case, it is naturally possible to properly combine ceramic members having different sizes, forms

powder as a solid content.

9. A ceramic structural body according to claim 7, wherein the silica-alumina ceramic fiber has a shot content of 1~10 wt% and a fiber length of 1~100 mm.

10. A ceramic structural body according to claim 7, wherein the silicon carbide powder has a particle size of 0.01~100 μm.

Fig. 2

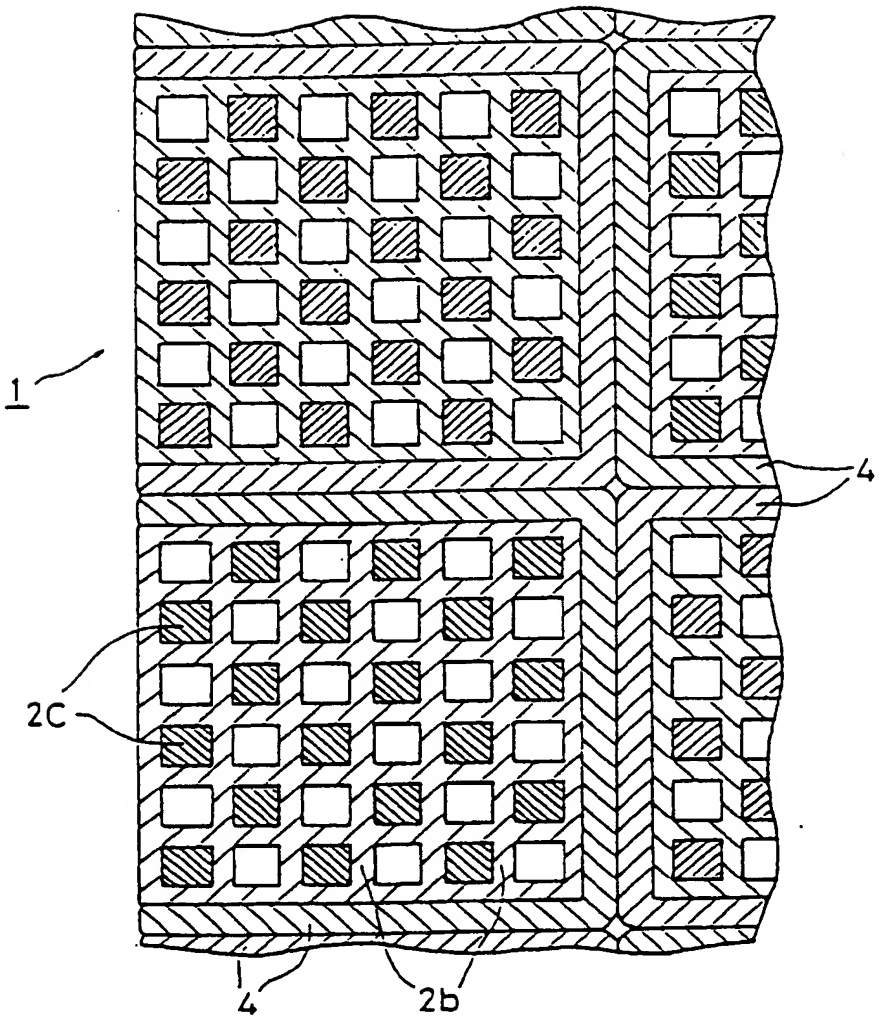


Fig. 4

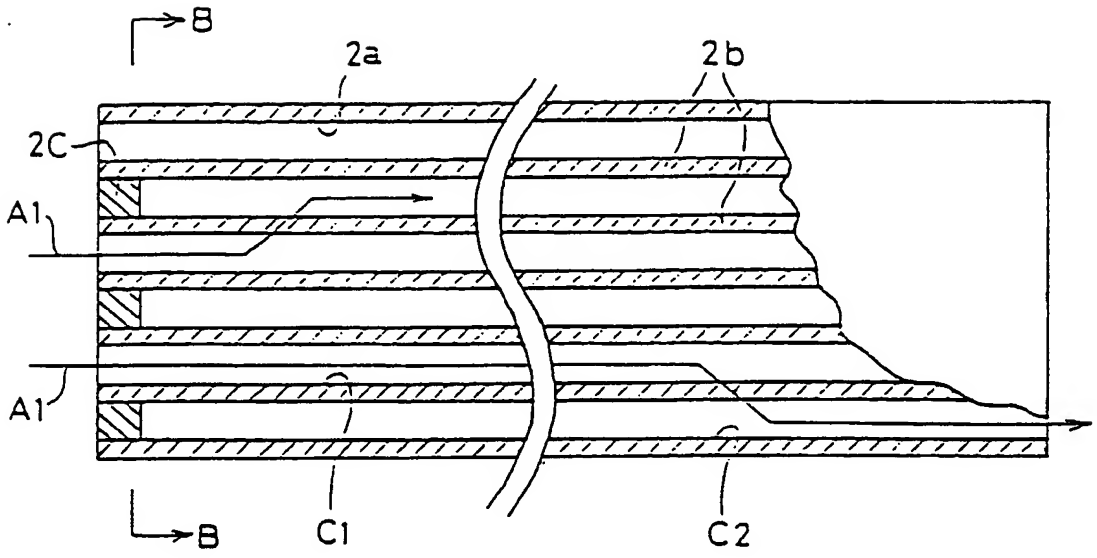
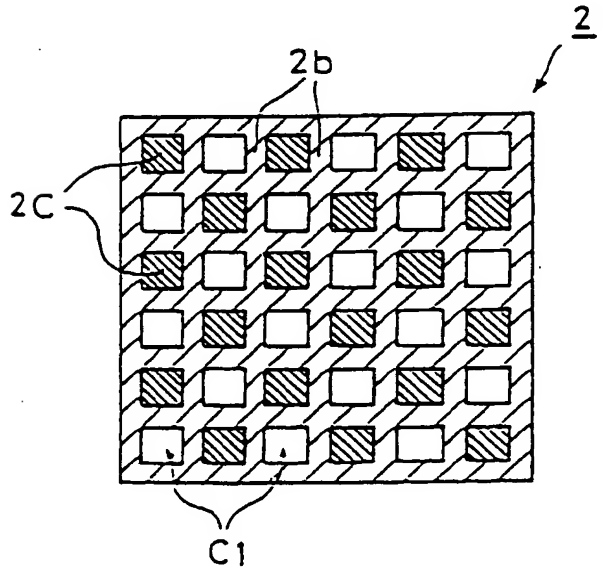


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/00042

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl^6 B32B18/00, F01N3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl^6 B32B18/00, F01N3/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926 - 1995
Kokai Jitsuyo Shinan Koho 1971 - 1995

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 7-54643, A (Ibiden Co., Ltd.), February 28, 1995 (28. 02. 95), Claim 4 (Family: none)	1 - 10
A	JP, 7-59885, B2 (Nippon Pillar Packing Co., Ltd.), June 28, 1995 (28. 06. 95), Claim & EP, 398130, A2	1 - 10
A	JP, 7-138533, A (Matsushita Electric Ind. Co., Ltd.), May 30, 1995 (30. 05. 95), Lines 38 to 41, right column, page 2 (Family: none)	1 - 10
A	JP, 5-115721, A (Matsushita Electric Ind. Co., Ltd.), May 14, 1993 (14. 05. 93), Claim 3 (Family: none)	1 - 10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
March 22, 1996 (22. 03. 96)	April 9, 1996 (09. 04. 96)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)